Vibrational Spectroscopy

Christian Hill

Remote Sensing Gone Wrong

THE ASTROPHYSICAL JOURNAL

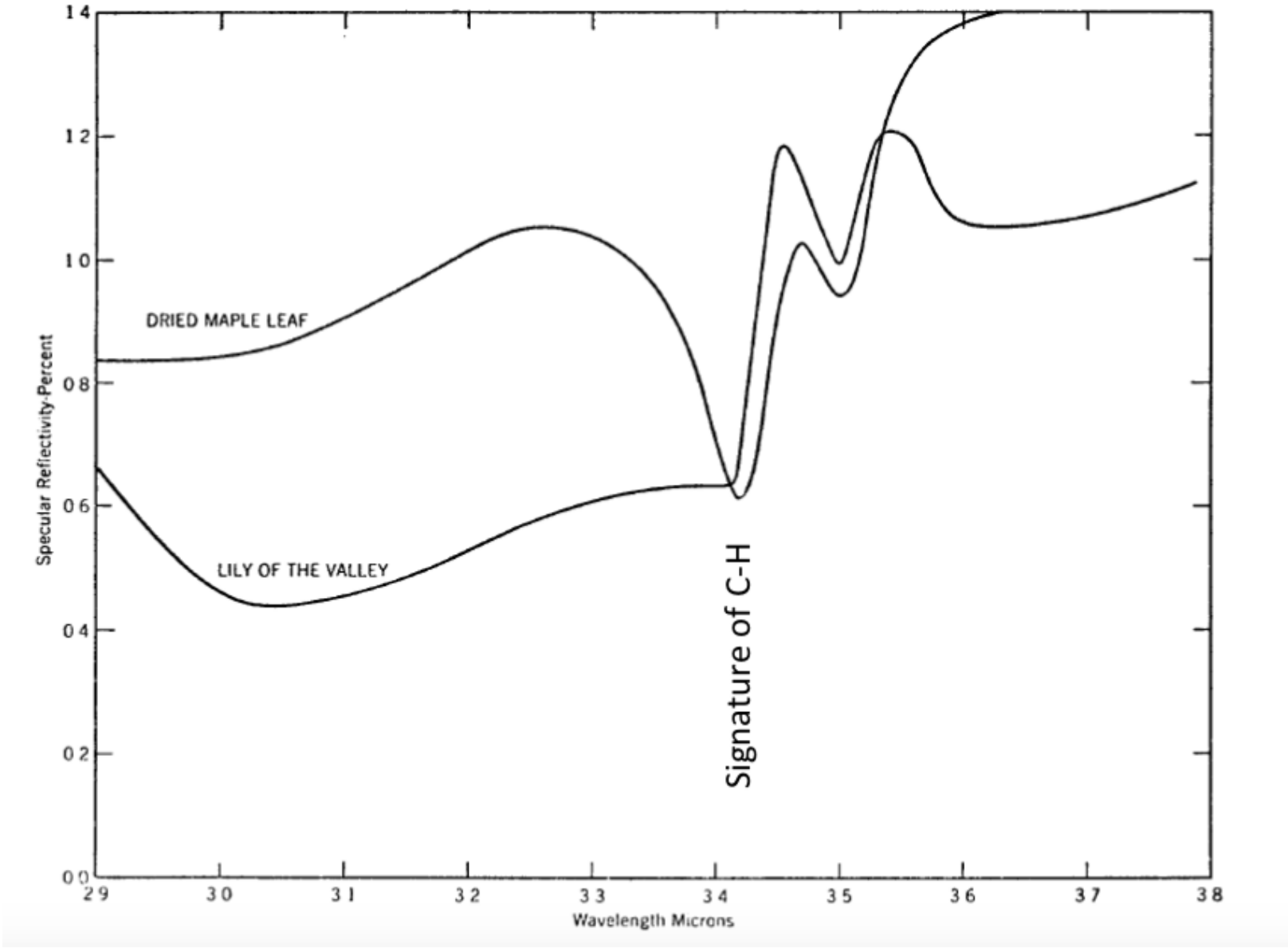
AN INTERNATIONAL REVIEW OF SPECTROSCOPY AND ASTRONOMICAL PHYSICS

VOLUME 126 SEPTEMBER 1957 NUMBER 2

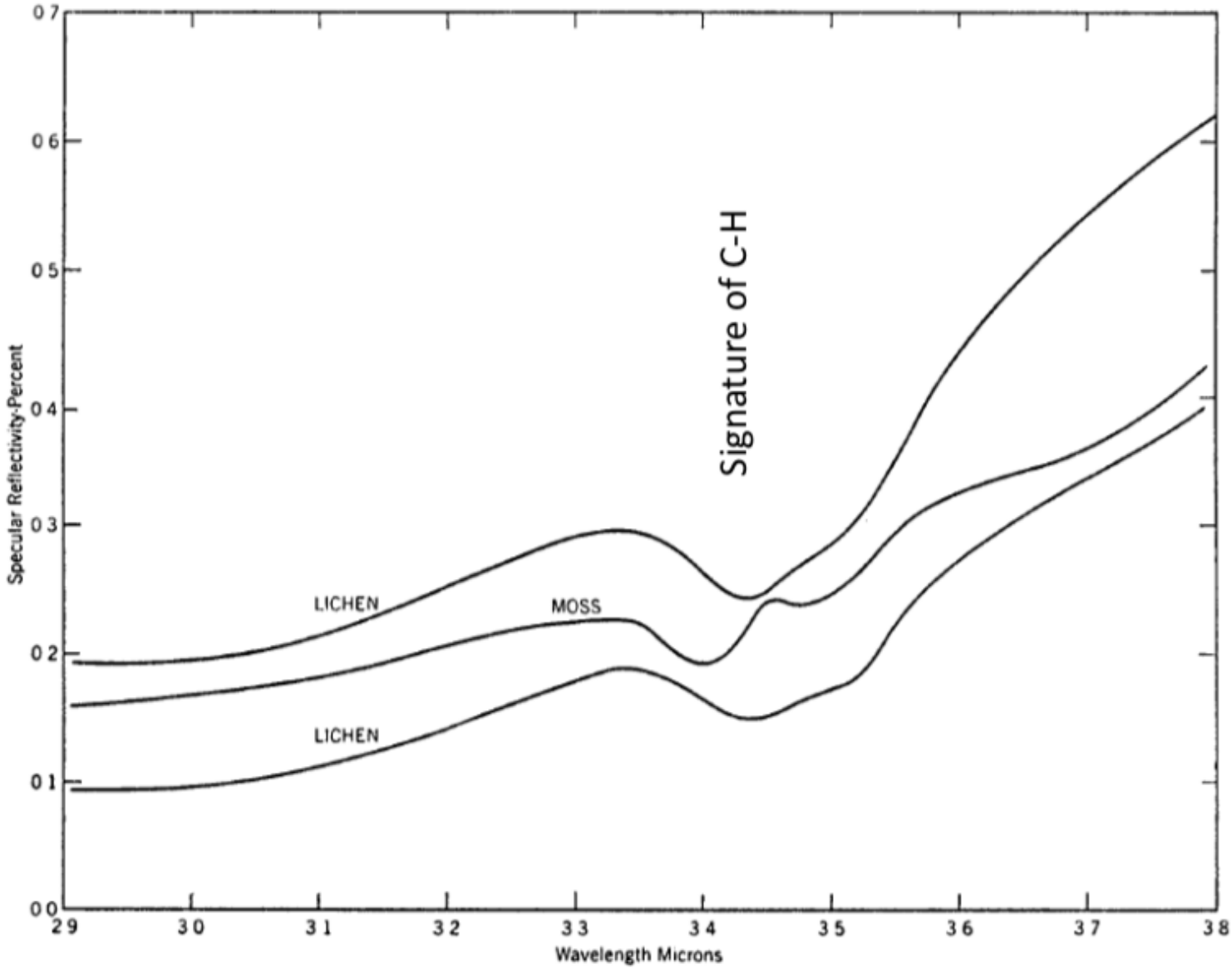
SPECTROSCOPIC EVIDENCE FOR VEGETATION ON MARS

WILLIAM M. SINTON
Smithsonian Astrophysical Observatory
Received May 6, 1957

Remote Sensing Gone Wrong



Remote Sensing Gone Wrong



Remote Sensing Gone Wrong

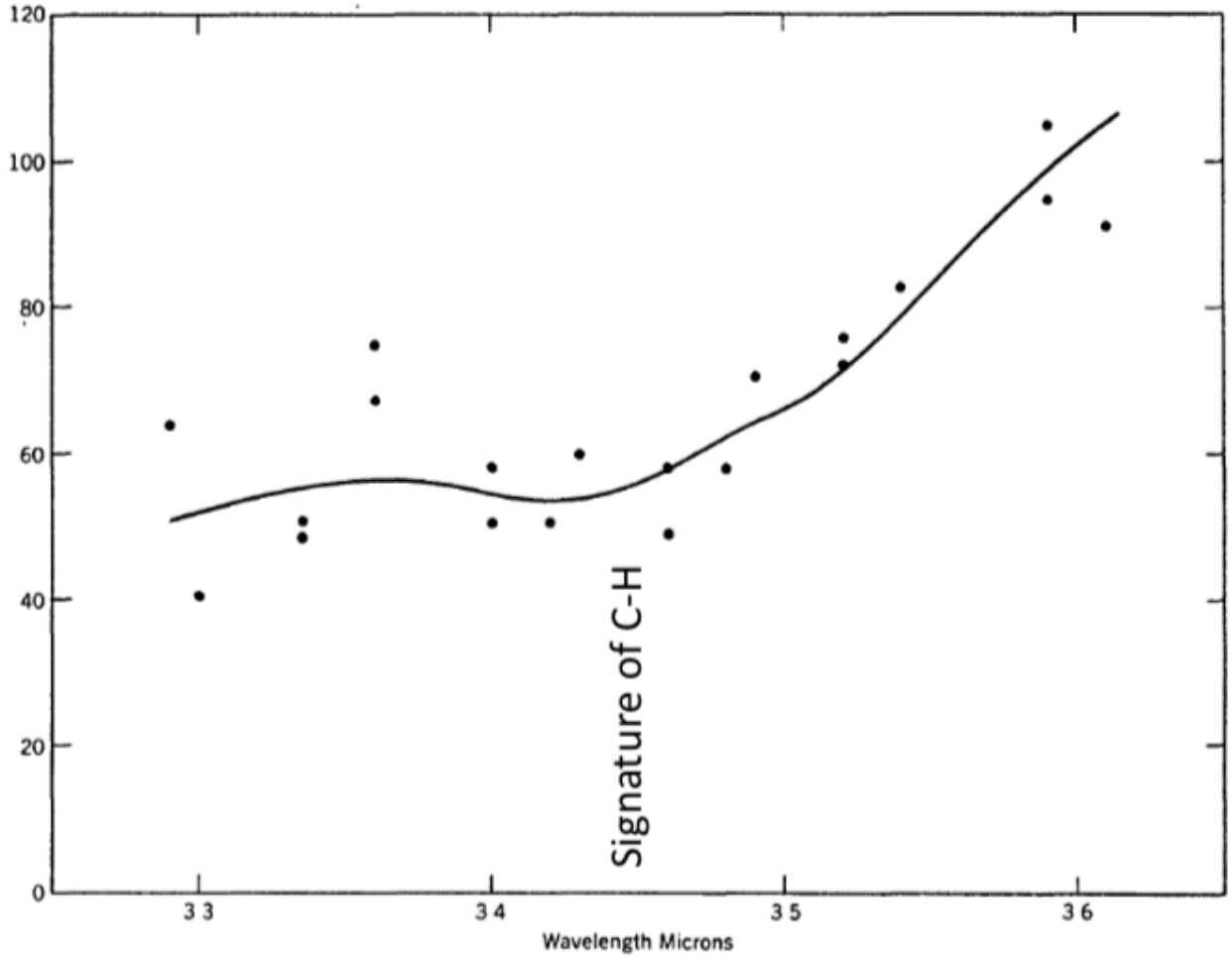
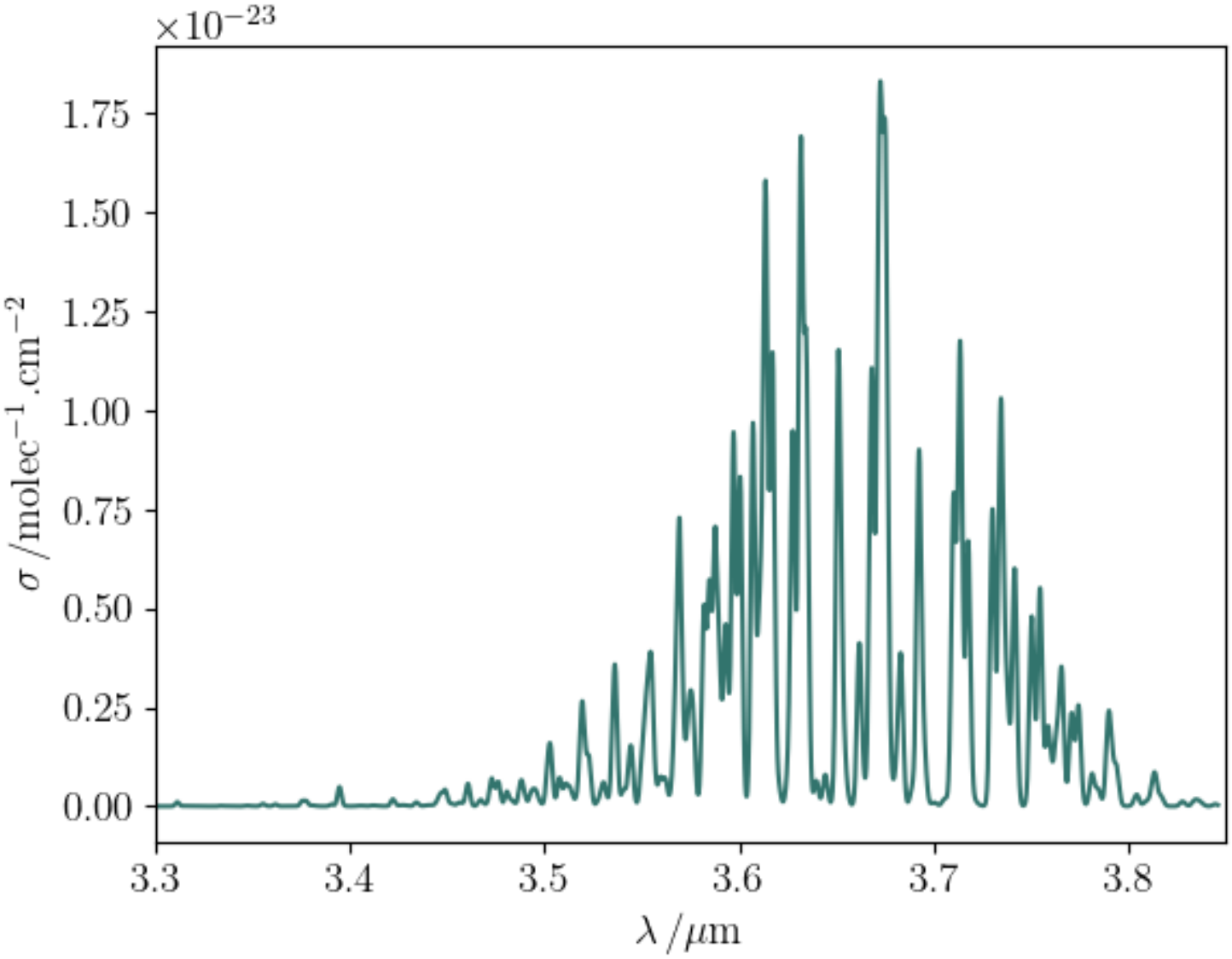


FIG. 3.—Observations of the spectrum of Mars obtained on four nights and after division by the solar spectrum (*solid curve* of Fig. 2).

Remote Sensing Gone Wrong



The Vibrational Hamiltonian

$$\nabla_R^2 S + \frac{2\mu}{\hbar^2}\left[E_{n,m} - V_n(R) - \frac{\hbar^2}{2\mu R^2} J(J+1)\right] S = 0$$

For the non-rotating molecule ($J = 0$):

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2 \frac{\mathrm{d}S}{\mathrm{d}R}\right) + \frac{2\mu}{\hbar^2}\left[E_{n,m} - V_n(R)\right] S = 0$$

$V_n(R)$ is in general a complex function that depends on the electronic wavefunction, but for small displacements from R_e:

$$V_n(R) = V_n(R_\mathrm{e}) + \frac{\mathrm{d}V_n}{\mathrm{d}R}(R - R_\mathrm{e}) + \frac{1}{2}\frac{\mathrm{d}^2 V_n}{\mathrm{d}R^2}(R - R_\mathrm{e})^2 + \ldots$$

The Vibrational Hamiltonian

$$V_n(R) = V_n(R_\mathrm{e}) + \frac{\mathrm{d}V_n}{\mathrm{d}R}(R - R_\mathrm{e}) + \frac{1}{2}\frac{\mathrm{d}^2V_n}{\mathrm{d}R^2}(R - R_\mathrm{e})^2 + \ldots$$

We can choose the first term to be zero.

The second term *is* zero.

Defining the *bond force constant*,

$$k = \left.\frac{\mathrm{d}^2V_n}{\mathrm{d}R^2}\right|_{R_\mathrm{e}}$$

we get $V_n(R) \approx \frac{1}{2}k(R - R_\mathrm{e})^2$

(the parabolic potential used earlier).

The Vibrational Hamiltonian

The resulting Schrödinger equation,

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}\left[E-\frac{1}{2}k(R-R_\mathrm{e})^2\right]S=0$$

can be solved exactly. Substitute $S(R)=\psi(x)/(x+R_\mathrm{e})$, where $x=R-R_\mathrm{e}$ is the displacement of the nuclei from equilibrium to get:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+\frac{1}{2}kx^2\psi=E\psi.$$

Harmonic motion with frequency $\omega=\sqrt{k/\mu}$.

The Vibrational Hamiltonian

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+\frac{1}{2}kx^2\psi=E\psi.$$

There is a characteristic length that we can scale x by: $\alpha=\hbar^p\mu^q k^r$ where the dimensions, $[\hbar]=[ML^2T^{-1}]$, $[\mu]=[M]$ and $[k]=[MT^{-2}]$. Since $[\alpha]=[L]$ we must have

$$\begin{aligned}L:1&=2p\\M:0&=p+q+r\\T:0&=-p-2r\end{aligned}$$

and hence $p=\frac{1}{2}, q=-\frac{1}{4}$ and $r=-\frac{1}{4}$:

$$\alpha=\left(\frac{\hbar^2}{\mu k}\right)^{1/4}$$

The Vibrational Hamiltonian

With the new coordinate, $q = x/\alpha = (\mu k/\hbar^2)^{1/4} x$ the Schrödinger equation is:

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q^2} - \frac{1}{2}q^2 = \frac{E}{\hbar\omega}\psi$$

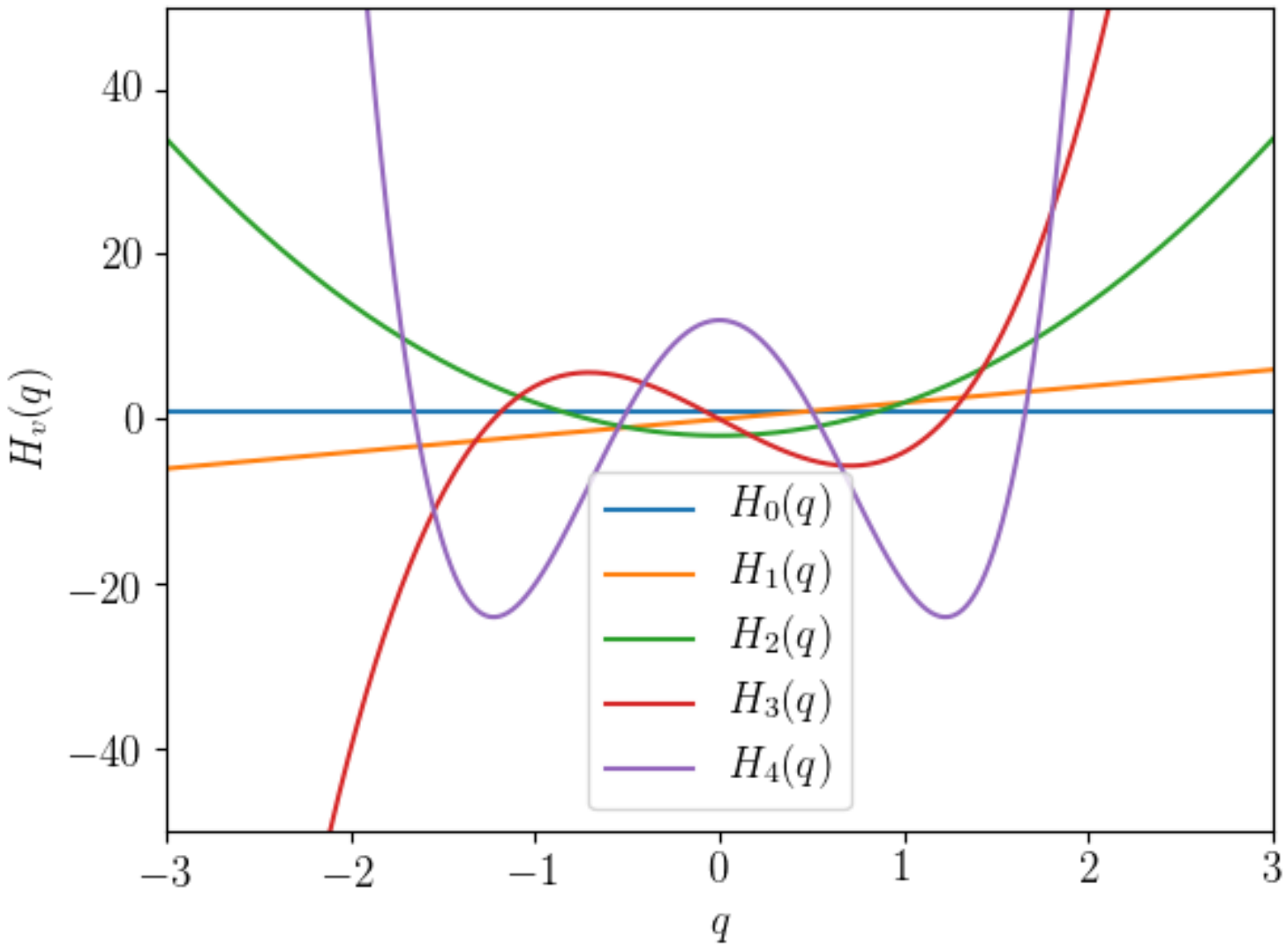
where $\omega = \sqrt{k/\mu}$ and its solutions are:

$$\psi(q) = N_v H_v(q) \exp(-q^2/2),$$

where $H_v(q)$ are *Hermite polynomials* and N_v is a normalization constant. The energy,

$$E_v = \hbar\omega(v + \tfrac{1}{2}) \quad \text{for } v = 0, 1, 2, \ldots.$$

Hermite Polynomials



Hermite Polynomials

- Definition:

$$H_v(q) = (-1)^v e^{q^2} \frac{\mathrm{d}^v}{\mathrm{d}q^v} \left(e^{-q^2} \right).$$

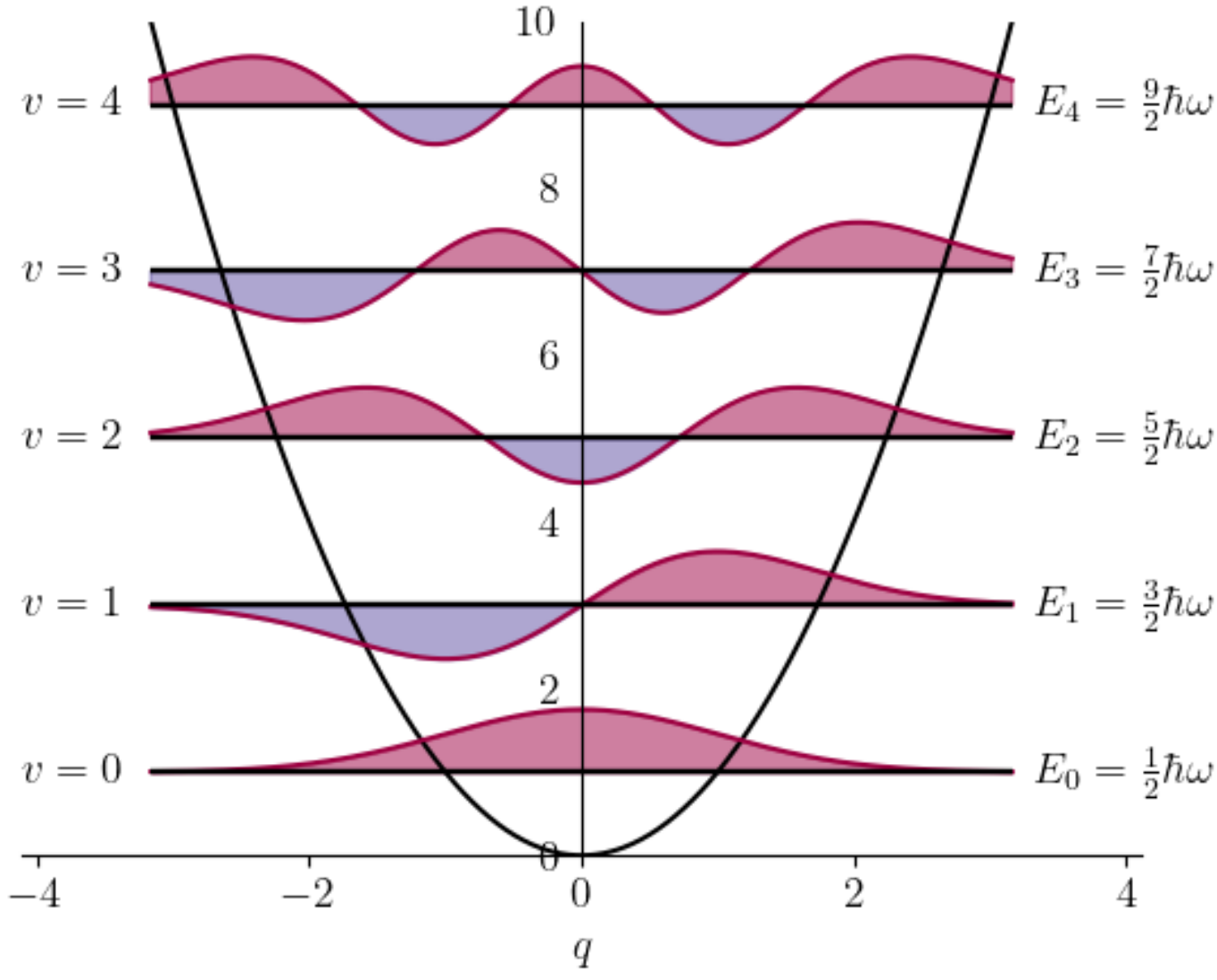
- Orthogonality with respect to weight function e^{-q^2}:

$$\int_{-\infty}^{\infty} H_m(q) H_n(q) e^{-q^2} \, \mathrm{d}q = \sqrt{\pi} 2^q q! \delta_{nm}.$$

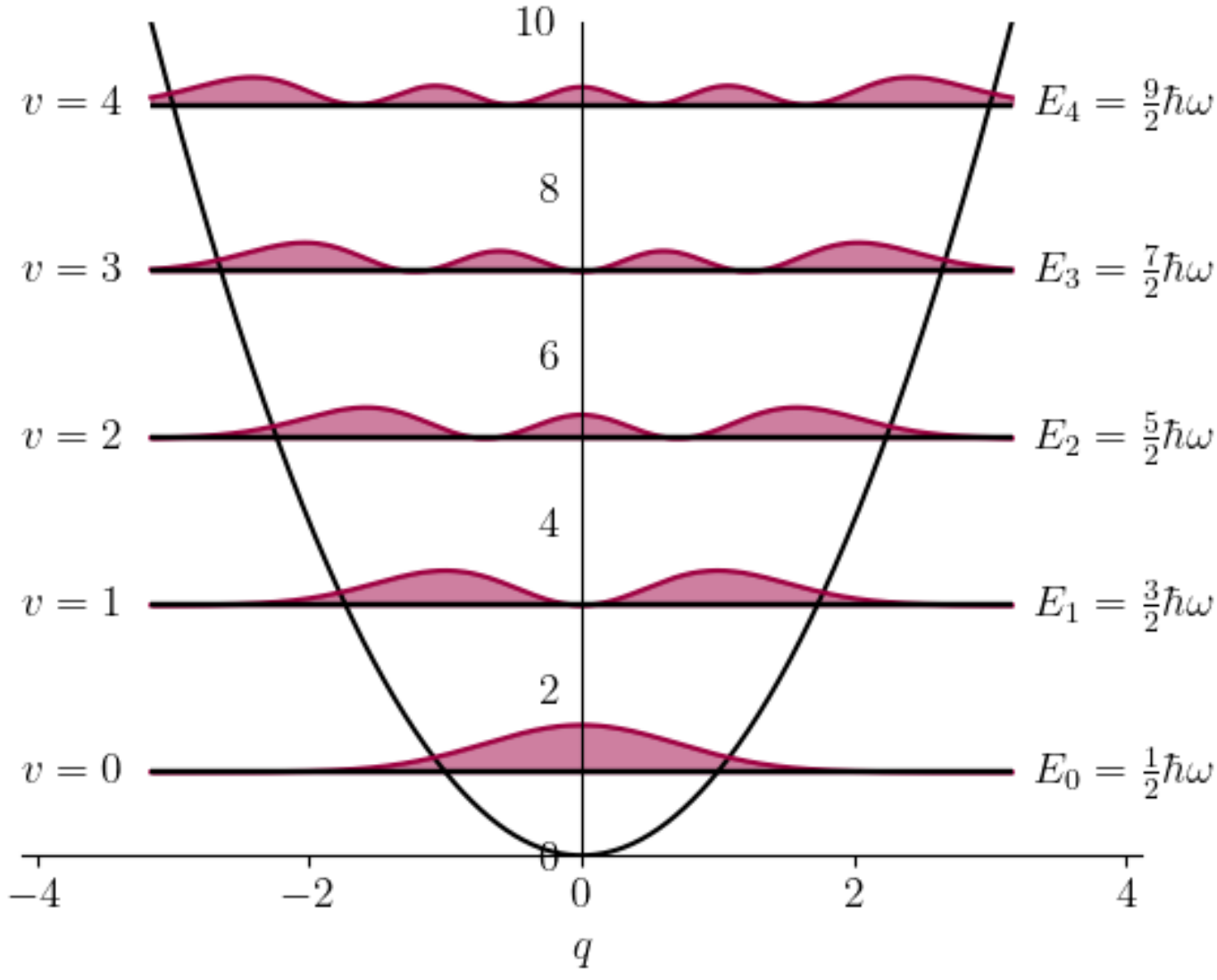
- Recursion:

$$H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q).$$

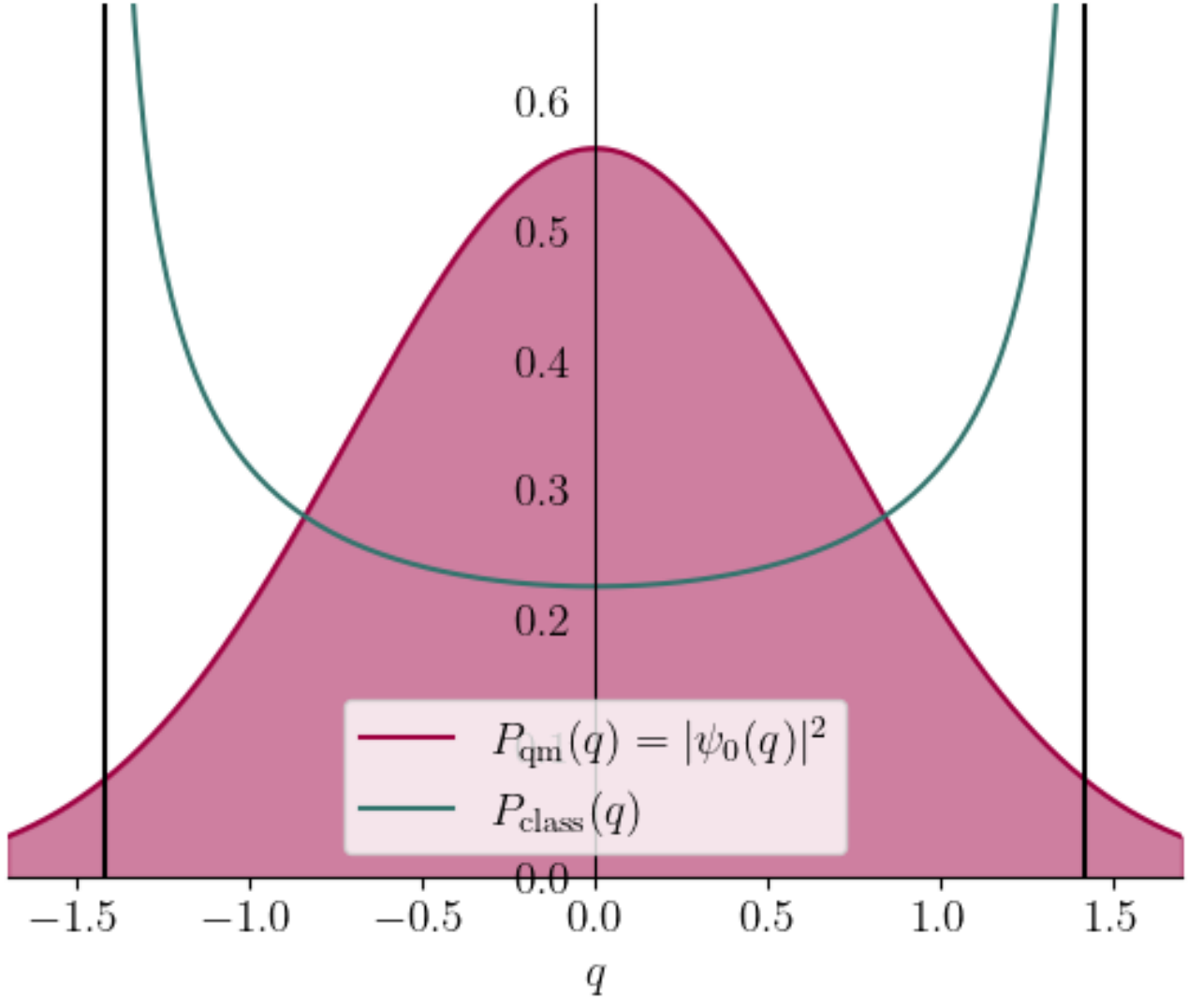
Harmonic Oscillator Wavefunctions



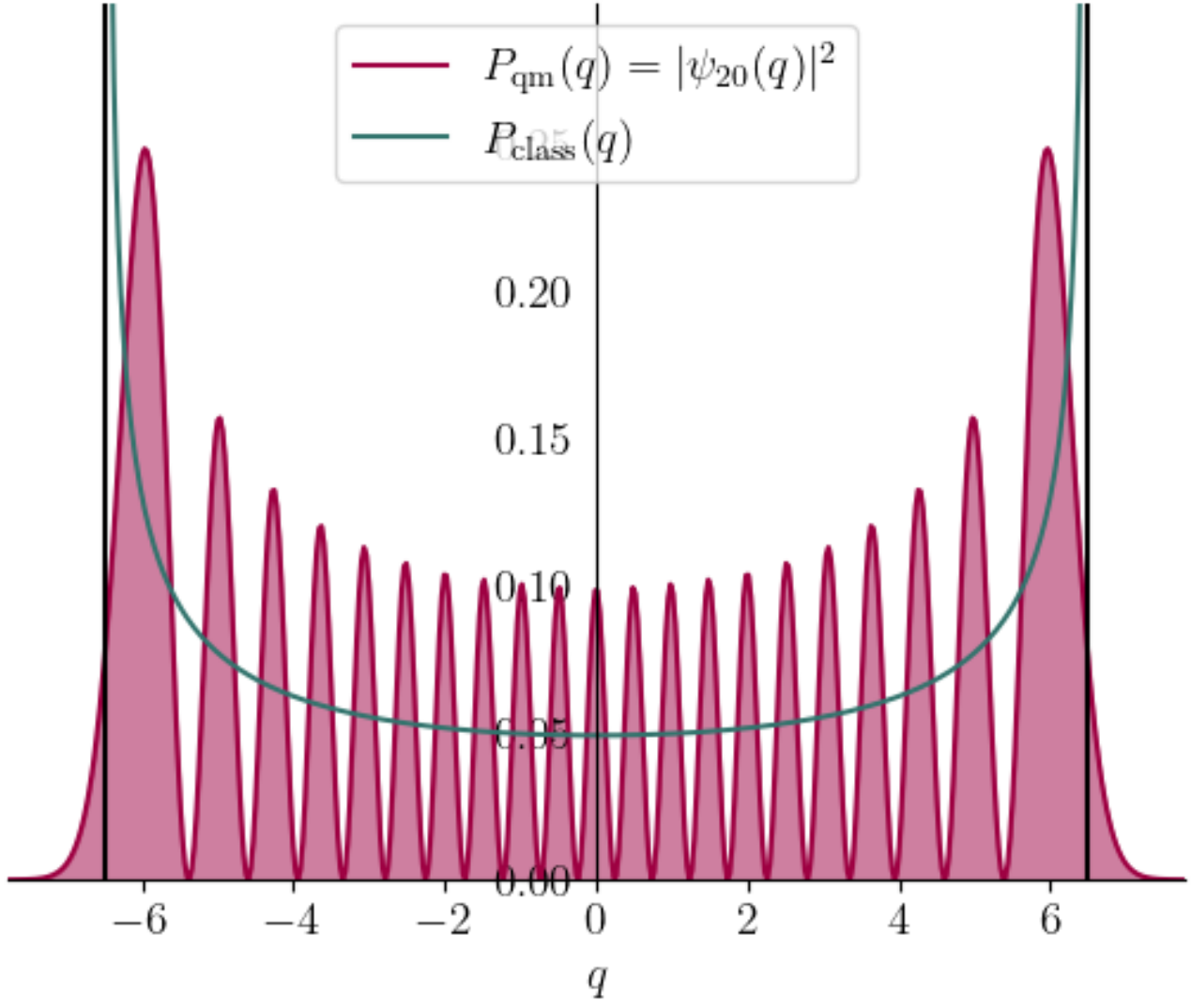
Harmonic Oscillator Probabilities



Harmonic Oscillator Probabilities



Harmonic Oscillator Probabilities



Vibrational Transitions

- The transition probability from one vibrational state, v'' to another, v', is the square of the *transition dipole moment*:

$$M_{v'v''} = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\mu}(q) \psi_{v''} \, \mathrm{d}q.$$

- The dipole moment operator is a complex function of q but may be expanded in a Taylor series:

$$\hat{\mu} = \mu_0 + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 q + \cdots$$

- Therefore,

$$M_{v'v''} \approx \mu_0 \int_{-\infty}^{\infty} \psi_{v'}^* \psi_{v''} \mathrm{d}q + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 \int_{-\infty}^{\infty} \psi_{v'}^* \cdot q \cdot \psi_{v''} \mathrm{d}q$$

Vibrational Transitions

$$M_{v'v''} = \mu_0 \int_{-\infty}^{\infty} \psi_{v'}^* \psi_{v''} \mathrm{d}q + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 \int_{-\infty}^{\infty} \psi_{v'}^* \cdot q \cdot \psi_{v''} \mathrm{d}q$$

The first term here is zero by orthogonality of the Hermite polynomials, leaving

$$M_{v'v''} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} H_{v''}(q) q H_{v'} \mathrm{d}q.$$

Using the recursion relation

$H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q)$:

$$M_{v'v''} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} \left[\frac{1}{2} H_{v''+1}(q) + v'' H_{v''-1}(q)\right] H_{v'}(q) \mathrm{d}q.$$

Vibrational Transitions: Selection Rules

$$M_{v'v''} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} \left[\frac{1}{2} H_{v''+1}(q) + v'' H_{v''-1}(q)\right] H_{v'}(q) \mathrm{d}q.$$

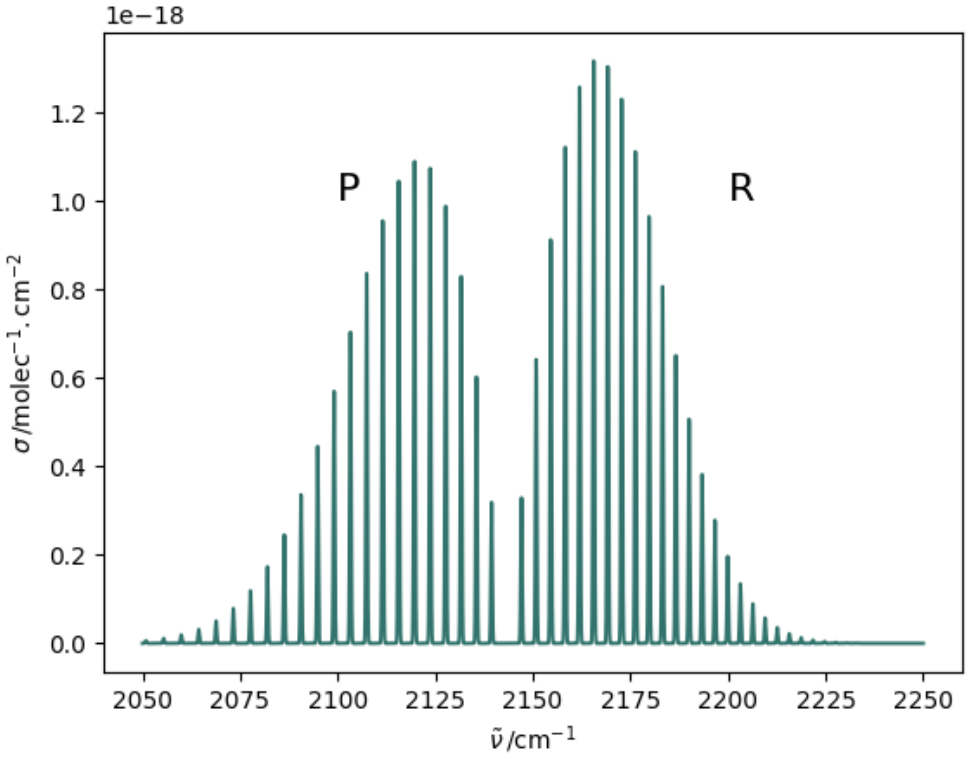
- *Gross selection rule*:

$$\left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 \neq 0$$

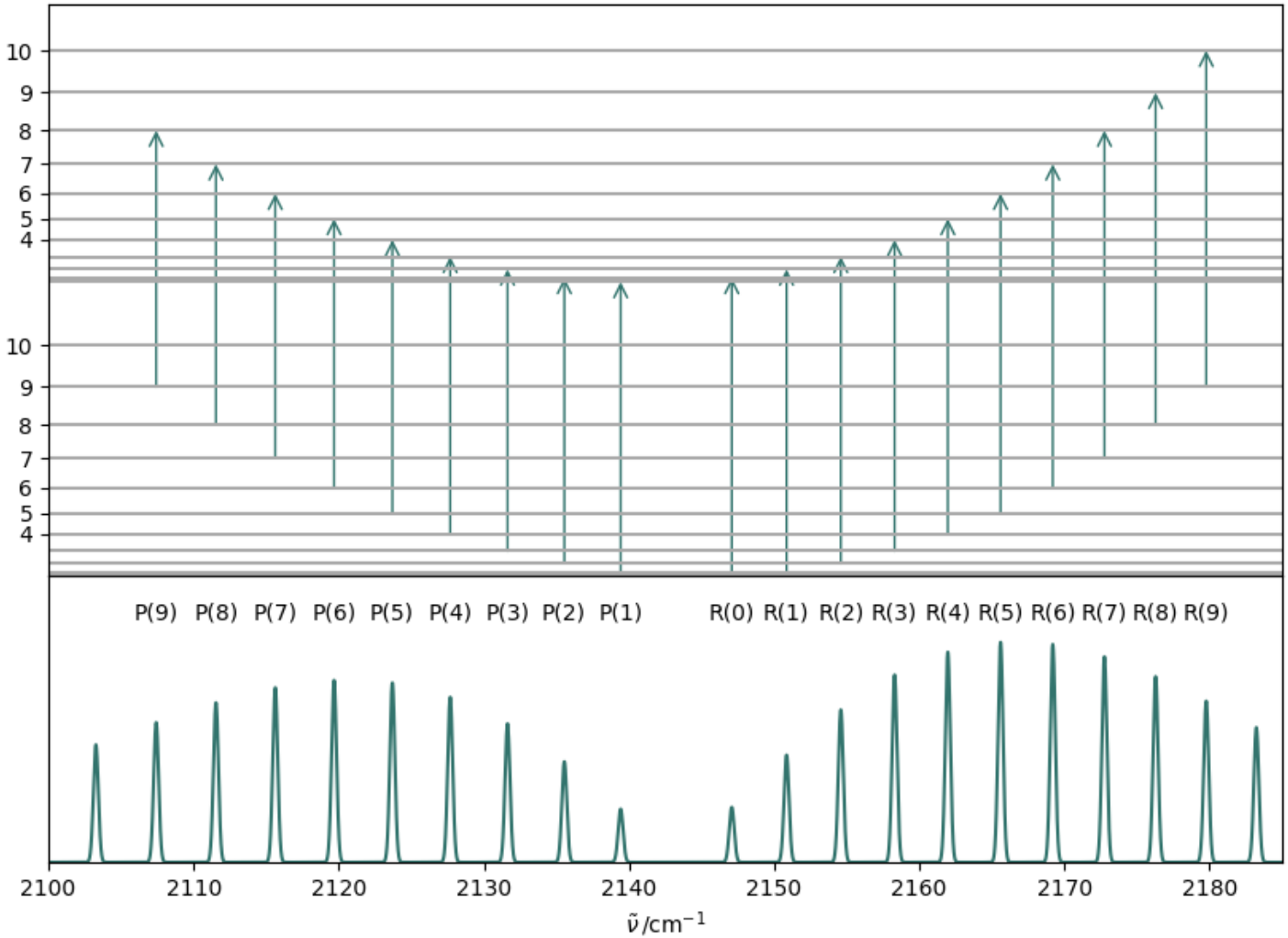
- $\Delta v = v' - v'' = \pm 1$
- NB homonuclear diatomics (e.g. H_2) do not have an (electric-dipole allowed) vibrational spectrum.

Rovibrational Transitions

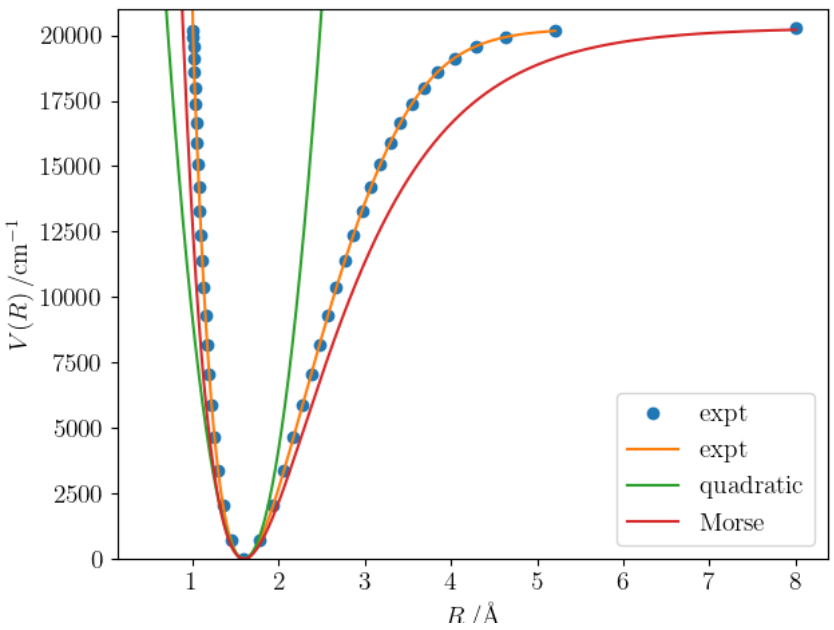
- Further selection rule on J: $\Delta J = \pm 1$
- P ($\Delta J = -1$) and R ($\Delta J = +1$) branches
- e.g. CO “fundamental” band: $v = 1 \leftarrow 0$

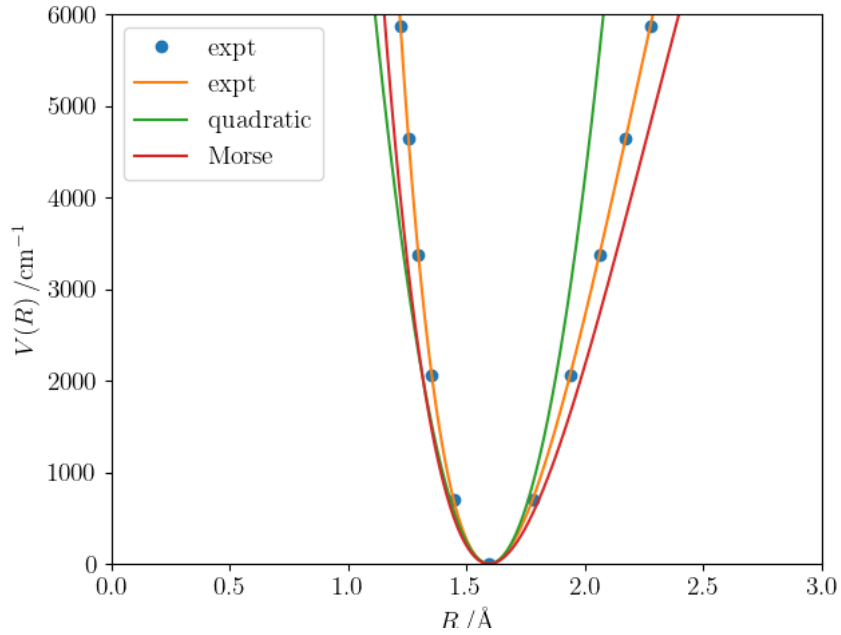


Rovibrational Transitions



Anharmonicity





- Real molecules dissociate
- Transitions with $\Delta v = \pm 2, \pm 3, \ldots$ are (weakly) allowed
- $v = 0 \rightarrow 2, v = 0 \rightarrow 3$ *overtones*

Vibration-Rotation Interaction

When a molecule vibrates its moment of inertia, $I = \mu R^2$ changes

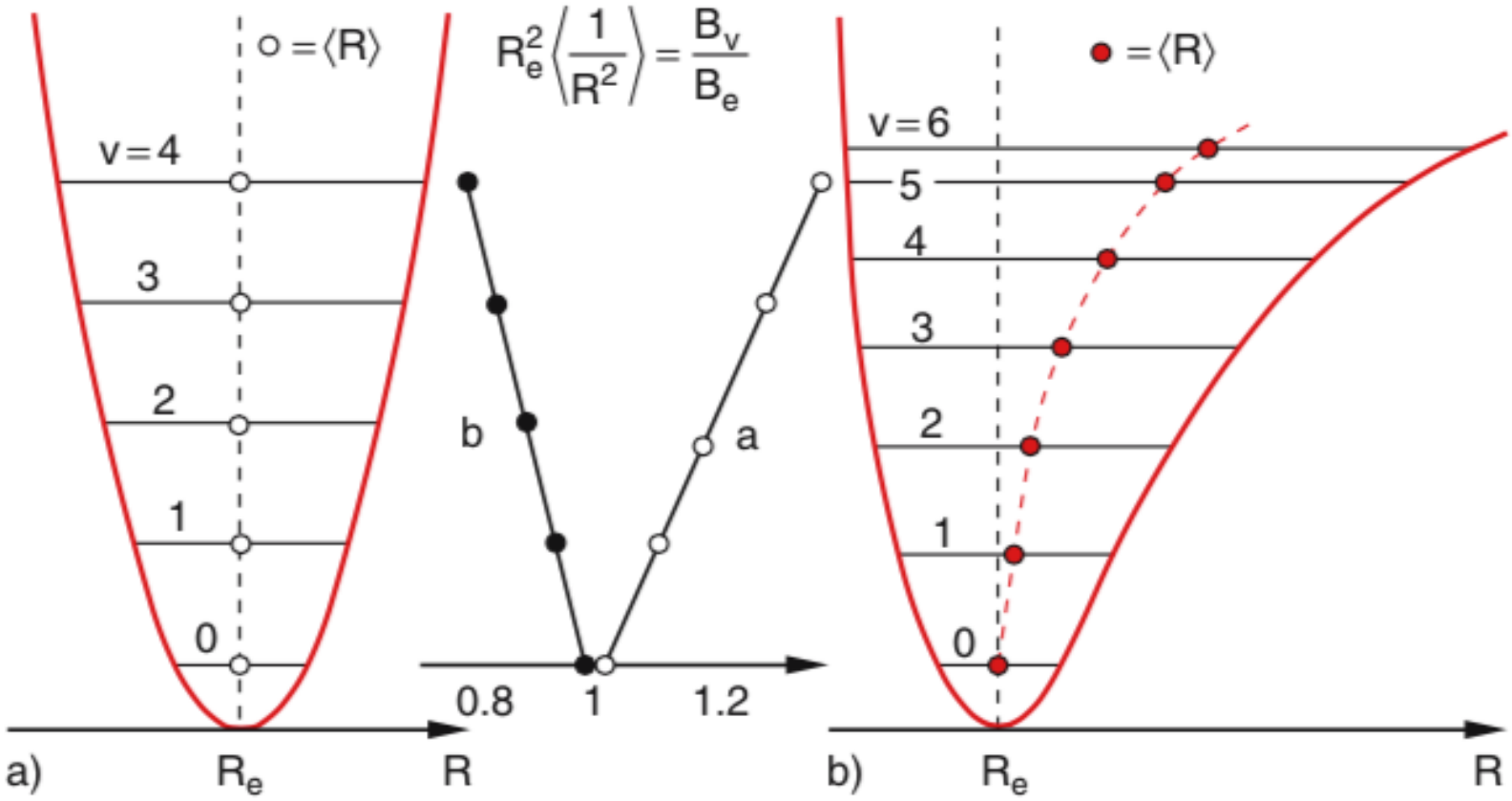
- The vibrational frequency is typically 10 – 100× faster than the rotational frequency
- Calculate the rotational energy using a time-average over a vibrational period:

$$\langle E_{\text{rot}}(J;\nu)\rangle = \frac{\hbar^2 J(J+1)}{2\mu}\left\langle \frac{1}{R^2} \right\rangle$$

where

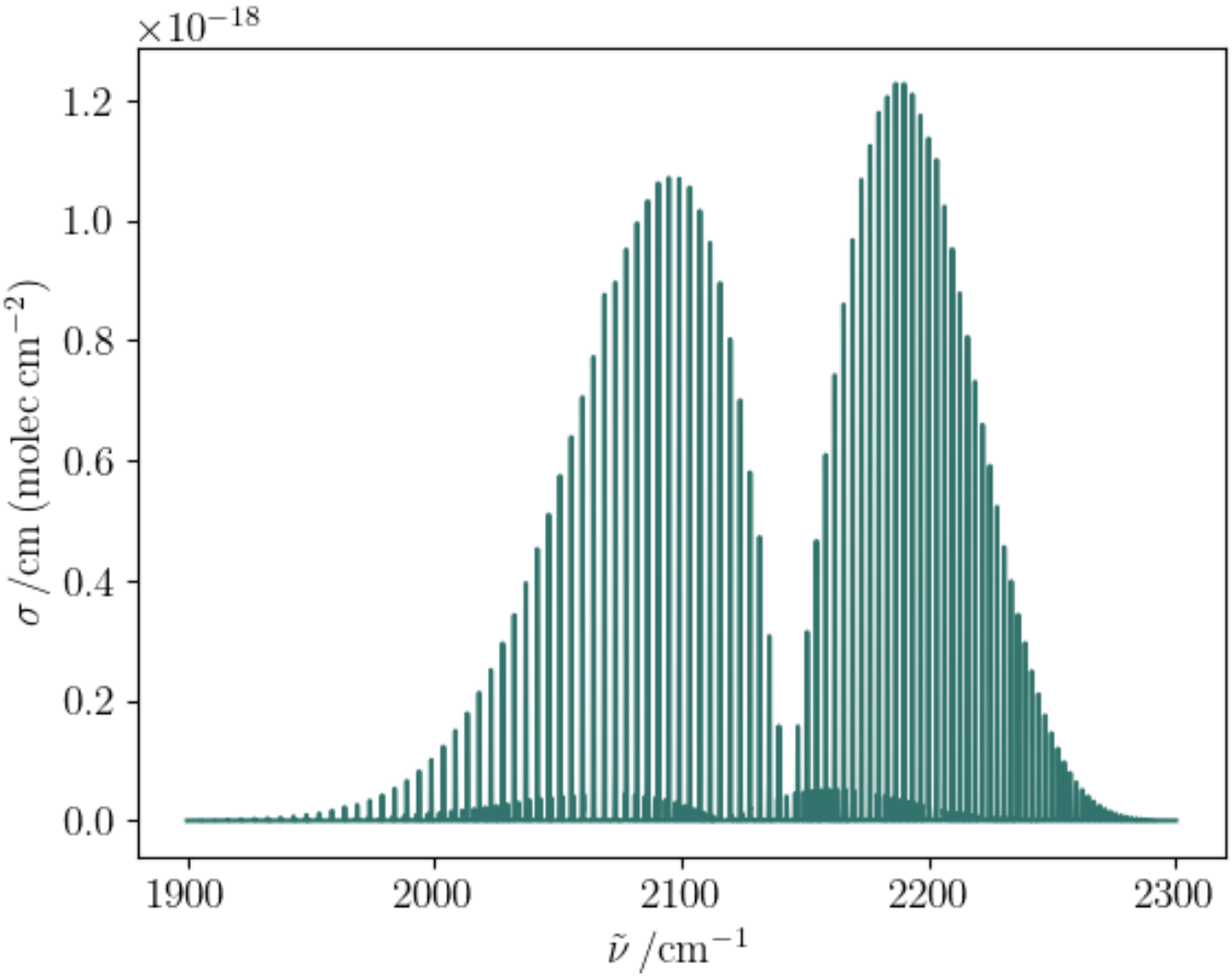
$$\left\langle \frac{1}{R^2} \right\rangle = \int_{-\infty}^{\infty} \psi_\nu^* \frac{1}{R^2} \psi_\nu \, \mathrm{d}R$$

Vibration-Rotation Interaction



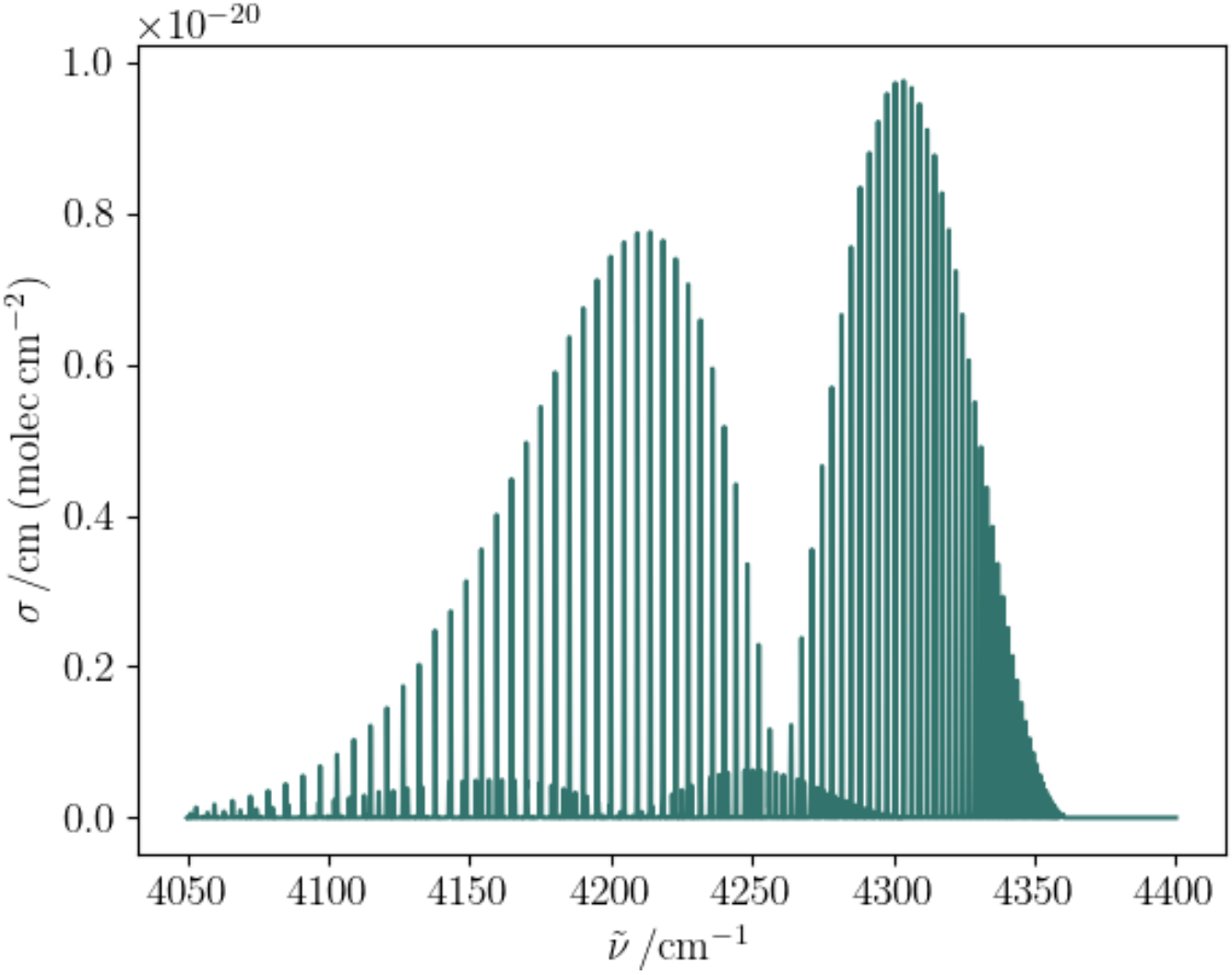
$$B_v = \frac{h}{8\pi^2 c\mu}\left\langle \frac{1}{R^2} \right\rangle = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2 + \cdots$$

Vibration-Rotation Interaction



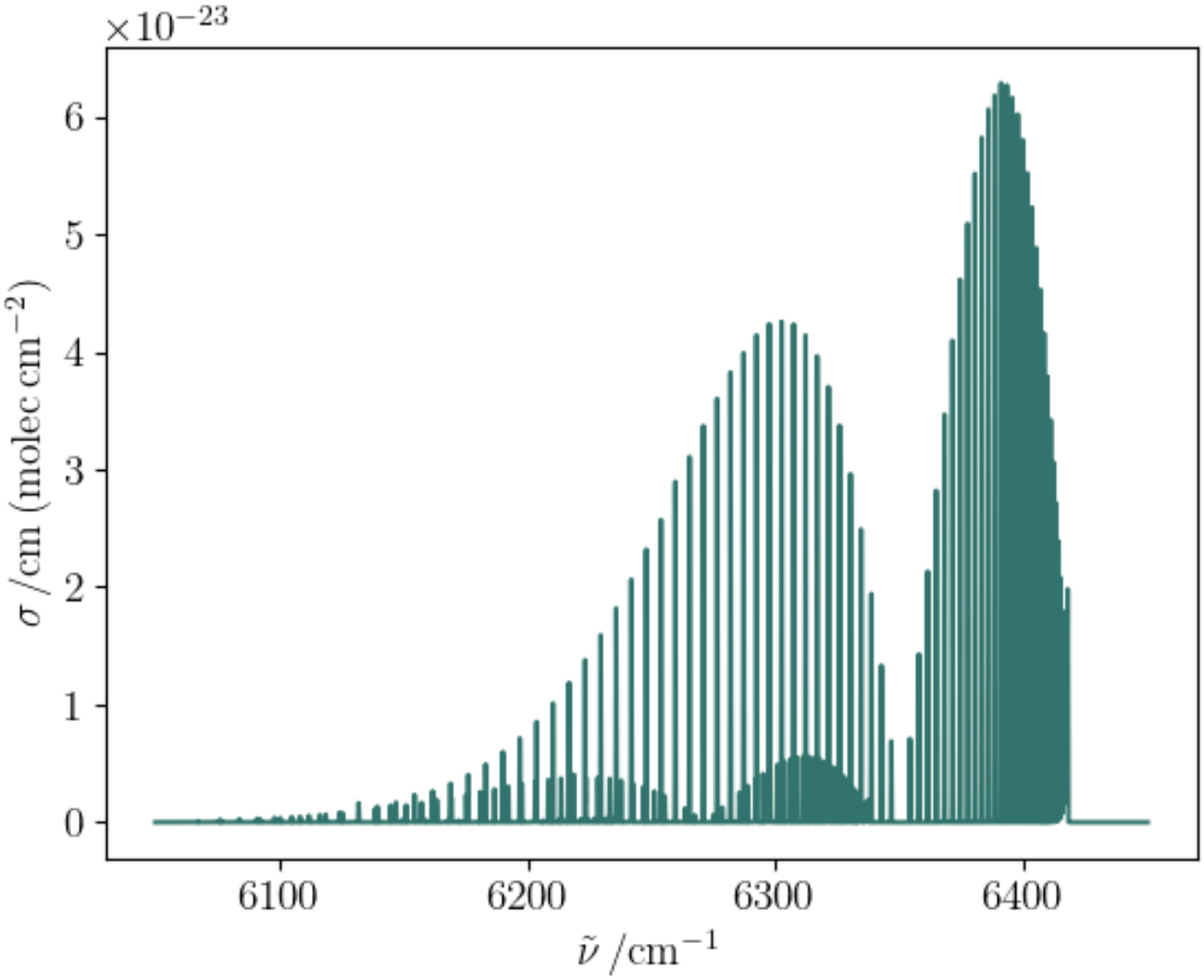
The 0-1 band of CO

Vibration-Rotation Interaction



The 0-2 band of CO

Vibration-Rotation Interaction



The 0-3 band of CO